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THE EFFECT OF FOOD SOILS ON THE STABILITY OF CHLORINATED DISHWASHING SOLUTIONS

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Army Natick Laboratories
Natick, Massachusetts

July 1973

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TECHNICAL REPORT

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UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing & Personal Life Support Equipment
Laboratory

C&PLSEL-106

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US ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

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FOREWORD

Many machine dishwashing compounds are formulated with organic chlorine-releasing compounds and contain from 1 to 2 percent available chlorine. The use of such compounds is said to prevent stain build-up on tableware and to assist in the removal of protein-type soils.

Laboratory tests were made to determine the relative chlorine stability of solutions of these dishwashing compounds in the absence and in the presence of oxidizable food soils.

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13. ABSTRACT

One of the federal specification machine dishwashing compounds and many of the commercial products contain chlorine-releasing compounds and have from 1 to 2 percent available chlorine. The active chlorine in dishwashing solution is said to prevent stain build-up on tableware and to assist in removing protein-type soils.

In tests conducted on chlorinated dishwashing compounds in Army mess halls, the active chlorine completely disappeared from the wash solution after about one-half hour of operation, even though the solution strength was maintained by the regular addition of dishwashing compound. Laboratory tests showed that this loss in available chlorine is attributed, at least in part, to a reaction between the chlorine and oxidizable food soils.

In the absence of an oxidizable food soil, the solutions of all of the dishwashing compounds tested were stable (only a slight loss in available chlorine) under the test conditions of high temperature (65°C) and vigorous agitation. However, when small amounts of salad dressing (170 ppm) were dispersed in dishwashing solutions, all of the dishwashing compounds showed a rapid depletion of available chlorine. To benefit from the use of a chlorinated dishwashing compound and to prevent the rapid depletion of available chlorine by a reaction with dispersed food soil, it is necessary to thoroughly pre-flush tableware before it is placed in a dishwasher. The manufacturers of commercial chlorinated dishwashing compounds do not sufficiently emphasize this precaution.

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ABSTRACT

One of the federal specification machine dishwashing compounds and many of the commercial products contain organic chlorine-releasing compounds and have from 1 to 2 percent available chlorine. The active chlorine in dishwashing solution is said to prevent stain build-up on tableware and to assist in removing protein-type soils.

In tests conducted on chlorinated dishwashing compounds in Army mess halls, the active chlorine completely disappeared from the wash solution after about one-half hour of operation, even though the solution strength was maintained by the regular addition of dishwashing compound. Laboratory tests showed that this loss in available chlorine is attributed, at least in part, to a reaction between the chlorine and oxidizable food soils.

In the absence of an oxidizable food soil, the solutions of all of the dishwashing compounds tested were stable (only a slight loss in available chlorine) under the test conditions of high temperature (65°C) and vigorous agitation. However, when small amounts of salad dressing (170 ppm) were dispersed in dishwashing solutions, all of the dishwashing compounds showed a rapid depletion of available chlorine. To benefit from the use of a chlorinated dishwashing compound and to prevent the rapid depletion of available chlorine by a reaction with dispersed food soil, it is necessary to thoroughly pre-flush tableware before it is placed in a dishwasher. The manufacturers of commercial chlorinated dishwashing compounds do not sufficiently emphasize this precaution.

THE EFFECT OF FOOD SOILS ON THE STABILITY OF CHLORINATED DISHWASHING COMPOUNDS

Introduction

One of the federal specification machine dishwashing compounds and many of the commercial products contain from 1 to 2 percent available chlorine. These dishwashing detergents contain organic chlorine-releasing compounds such as trichloromelamine, dichloro-dimethylhydantoin and sodium dichloroisocyanurate. According to the manufacturers, the active chlorine in dishwashing solutions provides a bleaching action to prevent stain build-up on tableware and assists in removing protein-type soils by oxidizing them to water-soluble amino acids.

Natick Laboratories personnel conducted dishwashing tests in Army mess halls on chlorinated dishwashing compounds. On several occasions, they reported a complete disappearance of active chlorine from the solution after about one-half hour of operation, even though regular additions of dishwashing compound were made to maintain the dishwashing solution at the desired concentration. This loss in available chlorine was attributed, at least in part, to the reaction of chlorine with oxidizable food soils in the dishwashing solution.

Tests were performed to determine the approximate rate of reaction.

Experimental Work and Discussion of Results

Four commercial and two specification dishwashing compounds were analyzed for available chlorine according to procedure 1 of the Appendix. The results are shown in Table I. One of the specification products (Compound No. 6) was not suitable for further testing because of its very low available chlorine content (0.1%). The remaining five compounds were evaluated for solution heat stability.

TABLE I

CHLORINATED DISHWASHING COMPOUNDS TESTED

Dishwashing Compound			Analytical Data	
Code No. (1)	Commercial or Specification	Type of Water For Intended Use	Alkalinity As NA_2O Percent	Available Chlorine Percent
1	Commercial	Hard	32.5	2.3
2	P-D-435	Soft	32.0	1.8
3	Commercial	Soft	24.0	1.1
4	Commercial	Soft	44.4	1.3
5	Commercial	Soft	41.4	1.2
6	P-D-435	Soft	36.7	0.1

(1) See Code Sheet for Identification of Dishwashing Compound

First of all, solutions of dishwashing compound No. 4, at a concentration of 0.2 percent, were evaluated for heat stability at a temperature of $64° - 66°C$. These solutions were prepared with and without added food soils such as cooking oils (Wesson and olive), and salad dressing (Miracle Whip). Three liters of these solutions were heated rapidly on a hot plate to 65°C. and then placed in a constant temperature water bath and vigorously agitated. Samples (2.0 ml.) of the solution were withdrawn when prepared (cold) and when heated to 65°C. for 0, 10, 20, 30, 40 and 60 minutes. These samples were analyzed for ppm available chlorine (Table II).

The solution without added food soil or other material was very stable, and the available chlorine content did not change even after 60 minutes of heating. The available chlorine content of the solution, containing 10 and 20 mls. of olive oil, was reduced to about half the original value after 30 minutes at 65°C. The available chlorine content of a solution containing 20 ml. of olive oil and 5 ml. of vinegar was reduced to zero in the time it took to heat the solution on the hot plate from 25°C. to 65°C. Similarly, the available chlorine content of a solution with 10 ml. of olive oil and 2 ml. of vinegar was reduced to 1 ppm by 30 minutes at 65°C. A solution with 5 ml. of cider vinegar had 0 ppm of available chlorine after 10 minutes heating. Cider vinegar is a dilute impure solution of acetic acid (about 5%) and contains small amounts of invert sugars, glycerine, carbohydrates, proteins, and coloring matter. The invert sugars are readily oxidized by the chlorine-releasing bleach even at room temperature.

The addition of a salad dressing which contains oil and vinegar had a similar effect upon the stability of these chlorine-releasing compounds. As little as 1.0 gram of salad dressing in 3000 ml. of solution resulted in a complete loss of available chlorine after 10 minutes at 65°C.

After the testing of dishwashing compound No. 4, tests were performed with all five dishwashing compounds to determine the heat stability of soil-free solutions and solutions containing 170 ppm (0.5 gram per 3000 ml.) of salad dressing. The results of these tests are listed in Table III. The soil-free dishwashing solutions were quite stable, losing on the average less than 2 ppm of available chlorine after 60 minutes at $64° - 65°C$. On the other hand, solutions with salad dressing lost between 91 and 94 percent of the available chlorine in 60 minutes at $64° - 65°C$. There is little difference between the commercial and specification dishwashing compounds for available chlorine stability in the presence of oxidizable food soils.

TABLE II

THE EFFECT OF HEATING ON THE AVAILABLE CHLORINE CONTENT OF SOLUTIONS OF A COMMERCIAL DISHWASHING COMPOUND No. 4* CONTAINING VARIOUS FOOD-TYPE SOILS

Food-Type Soils ** Added to the Dishwashing Solutions	Analysis of Dishwashing Solutions for Available Chlorine - PPM: Cold Solution (Before Heating)	Minutes the Solutions were Maintained at 64° - 66°C.: 0	10	20	30	40	60
None	23	23	23	23	23	23	23
Wesson Oil - 10 mls.	21	21	18	18	18	--	--
Olive Oil - 10 mls.	23	22	19	16	12	--	--
Olive Oil - 20 mls.	19	16	14	11	9	7	4
Olive Oil - 20 mls. Vinegar (cider) - 5 mls.	.6	0	0	--	--	---	--
Olive Oil - 10 mls. Vinegar (cider) - 2 mls.	18	8	5	3	1	--	--
Vinegar (cider) - 5 mls.	19	4	0	--	--	--	--
5% Acetic Acid - 5 mls.	16	15	13	14	13	12	12
5% Hydrochloric Acid - 5 mls.	15	15	14	13	13	13	11
Salad Dressing - 10 grams	13	1	0	--	--	--	--
Salad Dressing - 2 grams	18	0	0	--	--	--	--
Salad Dressing - 1 gram	19	5	0	--	--	--	--
Salad Dressing - 1/2 gram	18	8	4	1	0	--	--

* See Code Sheet for identification of dishwashing compound.

** These soils were dispersed into 3000 mls. of a 0.2% solution of dishwashing compound No. 4 at room temperature.

TABLE III

THE EFFECT OF HEATING ON THE AVAILABLE CHLORINE CONTENT OF SOLUTIONS OF DISHWASHING COMPOUNDS, SOIL-FREE AND CONTAINING 170 PPM FOOD SOIL

Code No. (1)	Dishwashing Compounds: Available Chlorine Percent (2)	Dishwashing Compounds: Solution Concentration Percent	Food Soil Present (3)	Analysis of Dishwashing Solutions for Available Chlorine - PPM: Solution Before Heating	Minutes Solutions were Maintained at 64° -66°C. (4): 0	10	20	30	40	60
1	2.3	0.2	No	36	35	--	33	--	33	34
1	2.3	0.2	Yes	35	24	18	13	9	5	2
2	1.8	0.2	No	32	31	--	30	--	30	31
2	1.8	0.2	Yes	30	21	14	11	8	5	2
3	1.1	0.3	No	32	31	--	28	--	31	32
3	1.1	0.3	Yes	31	23	18	13	11	7	3
4	1.3	0.2	No	26	25	--	24	--	23	22
4	1.3	0.2	Yes	25	15	10	6	5	3	2
5	1.2	0.2	No	23	22	--	22	--	22	22
5	1.2	0.2	Yes	21	16	10	7	5	3	2

(1) See Code Sheet for Dishwashing Compound Identification.
(2) Analysis of dishwashing compound as received.
(3) 0.50 grams Miracle Whip Salad Dressing in 3000 ml. of dishwashing solution (about 170 ppm).
(4) Dishwashing solutions were vigorously agitated by mechanical stirrer while the temperature was maintained by immersion of stainless steel beaker in a constant temperature hot water bath.

Conclusions

Manufacturers of commercial dishwashing compounds have stated that chlorine-releasing compounds in a dishwashing compound remove or prevent the build-up of stains on tableware and assist in the removal of soil by oxidizing protein-type soils to water-soluble amino acids. To fulfill this function, the amount of oxidizable food soils suspended in the dishwashing solution must be kept at a low level to prevent the rapid depletion of available chlorine by reaction with this dispersed food soil. To accomplish this, it is necessary to thoroughly pre-flush the tableware before it is placed in the dishwasher. If this is not done, the use of a dishwashing compound with a chlorinated ingredient is not worthwhile and represents a waste of material.

Appendix - Analytical Procedures

Analysis for Available Chlorine

Standard Test No. 50-B-100 - Monsanto Chemical Company

IODOMETRIC METHOD

A. SCOPE AND DISCUSSION

The determination is carried out by an iodometric method with titration to a starch end point with sodium thiosulfate solution.

B. EQUIPMENT

(1) 0 ml. burette

(2) 250 ml. Erlenmeyer flasks (500 ml. Erlenmeyer flasks)

(3) 100 ml. graduate cylinder (250 ml. graduate cylinder)

(4) 10 ml. graduate cylinder (25 ml graduate cylinder)

(5) Magnetic stirrer

(6) Teflon-covered stirring bar

(7) Distilled water wash bottle

(8) Analytical balance

C. REAGENTS

(1) 0.1 N. standard sodium thiosulfate solution

(2) 3% potassium iodide solution (iodate free)

(3) 2 N. sulfuric acid

(4) 1:1 sulfuric acid (Equal parts by weight H_2SO_4, sp. gr. 1.84, and distilled water)

(5) Starch indicator solution

(6) Reagent grade potassium dichromate, $K_2Cr_2O_7$

(7) Boric acid, H_3BO_3

(8) Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$

D. PREPARATION AND STANDARDIZATION OF SOLUTIONS

(1) Preparation of 0.1 N. Sodium Thiosulfate Solution

Clean a 1-liter glass stoppered bottle with cleaning solution and rinse thoroughly. Add 1 liter of distilled water to bottle. Add 25 grams reagent grade sodium thiosulfate crystals, $Na_2S_2O_3 \cdot 5H_2O$, and 2-3 grams borax crystals. (Borax is added as a preservative and makes a fairly stable solution.) Stopper the bottle and shake until all the solid is dissolved.

(2) Standardization of 0.1 N. Sodium Thiosulfate Solution

Accurately weigh out three portions of about 0.2 grams of potassium dichromate, $K_2Cr_2O_7$. Transfer each sample to a 500 ml. Erlenmeyer flask and dissolve in 100 ml. 2 N. sulfuric acid. (Prepare acid by adding 30 ml. concentrated H_2SO_4 to 500 ml. of distilled water.)

Add to each solution in small portions and with constant swirling, 2 grams powdered sodium bicarbonate and then pour in a solution of 10 grams iodate-free potassium iodide dissolved in 10 ml. of water. (The carbon dioxide evolved displaces air, thereby preventing air oxidation of iodide ion in the acid solution.) Swirl gently to mix, but avoid vigorous agitation. Use the specified weight of $NaHCO_3$ and allow to stand 5-10 minutes. (Time must be allowed for complete reaction. Longer standing is undesirable because of the possibility of air oxidation.)

Dilute each solution to 350 ml. (the final concentration of acid is about 0.4 N) and titrate with thiosulfate solution until the brown color of iodine begins to fade; then add 3-5 ml. of starch solution and complete the titration. At the end point, the blue color of starch-iodine disappears leaving the green color of the chromic ion.

From the weight of the dichromate used and the volume of thiosulfate, compute the normality of the latter. Average the three values obtained.

$$N = \frac{\text{wt. } K_2Cr_2O_7 \text{ (g.)}}{0.04904 \times \text{volume thiosulfate solution (ml.)}}$$

(3) Preperation of Starch Indicator

Stir 1-2 grams soluble starch with cold water to make a thick paste. Slowly pour this paste into 100 ml. of boiling water in which 1 gram of boric acid crystals has been dissolved. Continue boiling for 1 minute, then cool, and store in a stoppered bottle. Discard the preparation when it becomes cloudy or when it begins to give a reddish color with iodine.

E. PROCEDURE

(1) Analysis of Dishwashing Compounds

Using the analytical balance, weigh a 10-gram sample of dishwashing compound to the nearest 0.1 mg. and transfer quantitatively to a clean, dry 300 ml. Erlenmeyer flask containing a Teflon-covered stirring bar. Add 250 ml. of 3% potassium iodide solution to the flask and rinse down the walls of the flask with about 5 ml. water. Place the flask on a magnetic stirrer and stir until the sample is dissolved. Then add approximately 50 g. of crushed ice to cool the solution. Add slowly 25 ml. of 1:1 sulfuric acid. Titrate with 0.1 N. sodium thiosulfate to a light yellow color. Add starch indicator to give a deep purple color and continue to titrate slowly until the color just disappears. Record the volume of sodium thiosulfate solution used and calculate the available chlorine level according to the following formula:

$$\text{\% Available Chlorine} = \frac{\text{ml. thiosulfate} \times \text{N. thiosulfate} \times 0.03546 \times 100}{\text{wt. sample (g.)}}$$

The average available chlorine content is determined from three replicate samples.

(2) Analysis of Dishwashing Compound Solutions

Using a 200 ml. volumetric flask, transfer 200 mls. of dishwashing solution to a 300 ml. Erlenmeyer flask containing a magnetic stirring bar. To this flask add approximately 0.1 gram of potassium iodide crystal and 2 ml. of glacial acetic acid. Stir to dissolve and titrate solution with 0.1 N. sodium thiosulfate solution until yellow color starts to fade. Add about 1 ml. of starch indicator solution and titrate to the fade out of blue color.

$$\text{\% Available Chlorine} = \frac{\text{ml. Thiosulfate} \times \text{N. Thiosulfate} \times 0.03546 \times 100}{200}$$

$$\text{ppm Available Chlorine} = \frac{\text{\% available chlorine}}{.0001}$$

CODE SHEET

Dishwashing Compound Identification Code

Compound Code No.	Trade Name or Specification	For Use in Hard or Soft Water	Manufacturer or Compound
1	IMPACT	Hard	Economics Laboratory, Inc.
2	P-D-435 FSN 7930-985-6905	Soft	Washington Chemical Sales of Maryland
3	Kloro-Kol	Soft	DuBois Chemical Co.
4	Score	Soft	Economics Laboratory, Inc.
5	Acclaim	Soft	Economics Laboratory, Inc.
6	P-D-435 FSN 7930-485-6905	Soft	Washington Chemical Sales of Maryland